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Vapor Generation Methods for Chemical Warfare Agents

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13. ABSTRACT (Maximum 200 words) Several methods have been used to generate vapor streams containing controlled concentrations of chemical warfare agents or simulants for a number of applications, including investigations of physical properties (e.g., vapor pressure), detector calibration, filter performance, toxicology, environmental sampling, and characterization of the off-gassing hazard of unknown samples. Novel methods have been developed recently that are suitable for generation of low-volatility agents (e.g., VX) at high purity and direct generation of vapors (i.e., without dilution) at extremely low concentrations and flow rates. This report summarizes selected vapor generation methods with a discussion of the advantages and disadvantages of each.				
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PREFACE

The work described herein was authorized under Project No. 1E2WAA. This work was started in July 2000 and was completed in September 2000.

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Vapor Generation Methods for Chemical Warfare Agents

1 Introduction

Methods to produce and control streams of air, nitrogen, and other carriers with precisely controlled concentrations of chemical warfare (CW) agent or toxic industrial vapors are crucial for evaluating the performance of systems and equipment used to protect combatants who might be exposed to environments containing these materials. Examples of protective equipment that rely on these methods include vapor filtration and detection systems. Also, physical property measurement studies, including vapor pressure, adsorption equilibrium, and toxicity, are required to assess contamination spread and the resulting physical hazard assessments and rely on methods to generate and precisely measure the concentration and flow rate of streams tainted with various concentrations of these vapors.

Several well-known methods of vapor generation are effected by using direct contact of the liquid with a carrier gas stream. These include sparging, where the carrier gas, or a portion of it, is bubbled through the liquid, syringe injection of the liquid material directly into a carrier gas flow stream, and vapor saturation. A novel direct method that has been developed in our Laboratories uses solid-state vapor generation. This method exploits the use of vapors pre-adsorbed onto high-surface-area solids below the saturation capacity in order to greatly reduce the equilibrium vapor pressure of liquids and thus permit direct generation of vapors at low flow and concentration. "Indirect" methods, where a barrier is introduced between the liquid and vapor, include permeation, diffusion, and effusion.

A number of routine and novel methods for measuring the concentration of CW agents and simulants in carrier streams are in use. The more common methods will not be discussed in this report. One method that has been developed and implemented recently to measure ultra-low adsorption equilibrium vapor phase concentration will be discussed since it employs novel methodology. This method uses a unique combination of vapor concentration, gas chromatography, and flame photometric detection and is suitable for routine measurement of concentrations in the low- to mid-part-per trillion (ppT) range. It is likely that laboratory measurements will be possible at concentrations below the ppT range using the concentrator-GC-FPD method, although the ultimate limit depends on which vapor is under investigation.

2 Vapor Generation Methods

Several methods to generate controlled concentrations of vapors are in current use at the Edgewood Chemical Biological Center (ECBC) of the US Army Soldier Biological and Chemical Center (SBCCOM) and will be briefly described in this section.

2.1 Liquid Sparging

The most direct method of vapor generation is to bubble all or part of a carrier stream into a liquid reservoir. The vapor concentration in the resulting carrier stream depends on the vapor pressure of the liquid and the fraction of the carrier stream used for the sparger-generator. Rossin and co-workers⁽¹⁾ have used this method extensively to generate air streams containing CW agent simulants to characterize the destruction efficiency of low space-time catalytic oxidation reactors.

A complementary method, commonly referred to as an impinger or bubbler sampler, has been used extensively to measure the concentration of vapor streams containing CW agents. In this method, a solvent specific to the analyte of interest is used in the impinger, which traps the vapor as it bubbles through the solution. The resulting solution is then analyzed using routine methods. Multiple impingers are commonly used in series to assess the trapping efficiency.

2.2 Saturator

Two types of saturator are currently in use and will be described briefly. The first is a delta tube and is used for low-flow applications where high purity streams of low-volatility agents are required. The second is a more conventional multiple-pass saturator, which uses a high-surface-area coating to wick up the liquid to facilitate evaporation.

2.2.1 Delta Tube Saturator: The delta tube generation system described here is primarily used for testing of small detection devices in the laboratory^(2,3,4). The sparger or "bubbler" type generator described above is replaced by a triangular delta tube, and a small drop (e.g., 100 μ l) of agent is used. The carrier gas stream sweeps over the liquid surface rather than through it to carry the vapor for further dilution. A two-stage dilution technique can be employed depending on the target concentration range.

The delta tube generator system is constructed using commercially available components. Corrugated Teflon lines are used to minimize sorption losses and maximize installation flexibility. Swagelok fittings and glass ball-and-socket joints also facilitate connections.

Staged dilution extends the operating range to extremely low concentration levels while keeping the total flow volume low. Presently, analytical instrumentation limitations make it unnecessary to require more than a two-stage dilution for the most volatile materials of interest. For example, GB is one of the most volatile liquid chemical agents tested routinely. A single stage of dilution can produce a final concentration near 0.1 mg/m^3 when the delta tube is held at 0°C at a total dilution flow rate of 3 liters per minute. By adding a second stage dilution, the range of GB concentrations can be extended to below 0.0001 mg/m^3 while maintaining a final flow rate of three liters per minute.

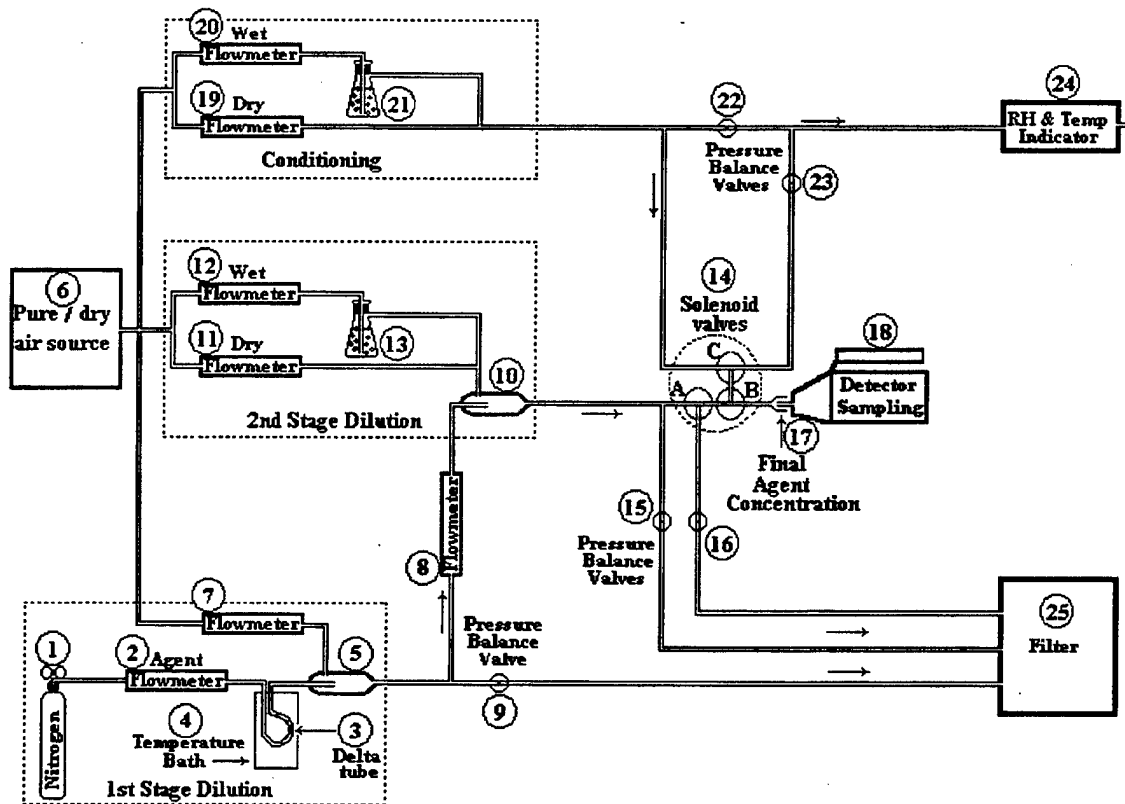


Figure 1. Flow Schematic of a Two-Stage Dilution Generation System with Optional Humidification

The flow schematic sketch in Figure 1 shows how the delta-tube generator system is configured. An air generator (AADCO Pure Air Generator) (6) provides the clean and dried (zero) air used for the carrier stream. This pressurized air is split into five streams each controlled by flow meters equipped with appropriate needle valves (7, 11, 12, 19, and 20). Flow meters (11), (12), (19), and (20) control the two controlled humidity dilution streams. These are identical for ease of operation. Flow meter (7) is used to provide a dry air stream for the first stage of dilution.

This two-stage dilution system provides an easily controlled low concentration level generation when limited air flow is required. The carrier gas for the first dilution is supplied from a nitrogen tank (1) and is controlled by a fine needle valve flow meter (2) into the agent reservoir or delta tube (3). The delta tube is immersed in a temperature-controlled bath (4) to maintain a constant temperature. The nitrogen carries the chemical vapor as it sweeps over the chemical and proceeds into a glass manifold (5) where it is met with a stream of dry air from the pure air generator through flow meter (7) to provide the first stage of dilution.

A portion of the resulting agent vapor flow is forced through a flow control meter (8) and valve (9) into manifold (10). It is met and further diluted with the humidity-tempered air from the combined streams from flow meters (11) and (12), as desired. The resulting RH is controlled by varying the ratio of the dry air (0% RH) from flow meter (11) and the wet (100% RH) air stream from flow meter (12) bubbling through the humidifier water reservoir (13). The RH is estimated by calculation and is compared with the RH and temperature indicator (24) installed in the conditioning air of the system. The humidified chemical vapor air stream is then split into two streams. One stream is directed to the solenoid valve assembly (14) consisting of three 3-way solenoid valves. The second stream is directed through a regulating valve (15) into a charcoal canister (25) to remove excess toxic chemical vapor.

A sample port (17) is connected directly to the solenoid assembly to minimize the delay when switching from conditioning air to the agent air during a challenge. The glass cup has slots to release the excess flow that is delivered to the detector inlet area. The detector samples the agent vapor without having to attach directly to the sample port. Usually, the delivered flow is approximately 2X the detector demand to insure that the detector is not starved. This approach precludes detector response pressure biasing.

The generation technique described previously has provided a successful means to generate VX vapor that is relatively free of its associated impurity vapors⁽⁴⁾ and has been used extensively for detector testing. A brief discussion of the VX generation technique is included here because of the unique behavior of VX and VX analogs with similar vapor pressure. To obtain purified VX vapor, a small amount of high purity VX agent is used in the delta tube. Contaminated VX vapor is produced when the generator is freshly charged owing to the higher volatility of impurities relative to VX. The vapor constituents vary with time as the sweeping air stream purges the sample. The starting CASARM (Chemical Agent Standard Analytical Reference Material) VX with purity of 95-98% contains a small percentage (2-5%) of impurities. One of the most notorious components, diisopropylaminoethyl mercaptan (thiolamine), for

example, has been found to interfere with many chemical detection devices as well as most analytical methodologies used for VX concentration determination. It has much higher volatility than VX (estimated volatility, 2130 mg/m³ versus 7.38 mg/m³ for VX at 20°C⁽⁵⁾). Therefore, although it only represents a small portion of the sample in the liquid state, it becomes the major constituent in the initial vaporized state and must be eliminated in order to generate purified VX vapor.

The approximately 300-fold difference in volatility permits purging of this impurity to rid of the diisopropylaminoethyl mercaptan, and other high volatility components can be purged similarly. Dry air or nitrogen is swept over the VX surface to carry the vapor for dilution to the necessary concentration. As the purging proceeds, the VX mole fraction in the effluent increases significantly for the small samples used in this work. It requires four to twelve hours of purging to achieve a VX mole fraction of higher than 95% in the effluent stream. The ultimate vapor purity depends on the amount, initial purity of VX, purging conditions such as temperature, time, and carrier flow rate. The normal procedure used by the ECBC, Design Evaluation Laboratory using the delta tube method and approximately 100 microliters of CASARM grade VX was to allow an overnight purging at 100 standard cubic centimeters per minute (sccm) at room or slightly elevated temperature (40°C). The purified VX will generally be useful for several days of testing before degrading. Although the exact cause of this degradation is unknown, small amounts of water vapor entrained in the carrier gas stream probably cause the VX to hydrolyze over time.

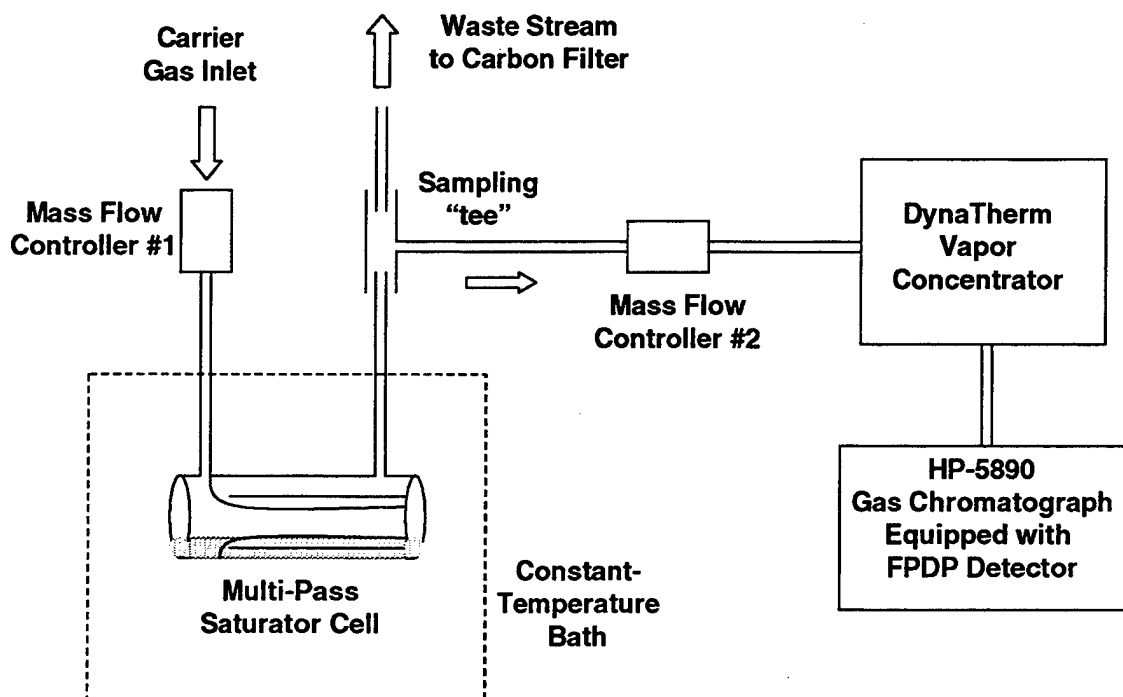


Figure 2. Large-Scale Saturator Cell

2.2.2 Large-Scale Saturator: A device similar to the delta tube has been developed and implemented recently to generate vapors for various applications including physical property (vapor pressure) measurements and filter testing ⁽⁵⁾. The larger version is shown schematically in figure 2. It is fabricated of concentric glass and ceramic tubes up to five cm in diameter and 15 cm long and has been used to generate flow rates up to 10 liters per minute. The larger systems can be scaled down to less than 0.1 liter per minute flow rate and can hold up to 100 g of liquid. These larger generators and liquid samples make it more difficult to purify low-volatility agents such as VX, however they have proven to be extremely stable and easy to operate. Large-scale saturators have been used extensively to generate challenge streams for CW agent and simulant studies where as much as 10 grams per experiment are needed to assess filtration performance.

2.3 High-Pressure Injection

During recent lab- and sub-scale tests of a pressure-swing adsorption (PSA) filtration system ⁽⁶⁾, it became necessary to inject a controlled mass (dose) of medium-volatility vapors, including nerve agent GB, into a high-pressure, high-flow feed stream and ensure evaporation prior to filter entry. This objective was accomplished by injecting liquids into a large (200-gallon) mixing chamber and pressurizing it to the feed condition (ca. 65 psig), allowing sufficient time for the liquid to evaporate and mix prior to injection. After preparing the premixed sample, the experiment was initiated as usual by feeding high-pressure air to the PSA feed stream. Once the PSA system achieved steady state at the desired feed humidity, the flow was diverted through the mixing chamber prior to entering the PSA test rig. Similar methods are applicable to pressurized or condensed vapors with suitable physical properties, i.e., suitable volatility.

2.4 Diffusion/Effusion

Diffusion is a steady state method that allows generation of vapors at levels lower than saturation values by limiting the contact between the liquid and carrier. For example, an open container can be placed at one end of a container while the carrier is passed through the other end. Vapor generation rate will depend on how fast diffusion occurs, which is related to the molecular mass of each, as well as the vapor pressure of the material, as well as the geometry and dynamics of the system. Another geometry that can be used is similar to effusion, but uses a barrier, e.g., drift tube between the sample cell and carrier stream to reduce the vapor flux.

Effusion is effected by encapsulating a sample with a fixed, thin orifice. This method has been used to measure the vapor pressure of solids and liquids since the effusion rate depends only on the size of the orifice and sample temperature, assuming that the vapor concentration in the vicinity of the orifice is kept low relative to the equilibrium concentration within the sample container. The latter condition is fulfilled whenever the sample container is maintained in an environment that will sweep away the effusing vapor, i.e., in vacuo or in a flow stream. These methods are not currently used extensively at ECBC.

2.5 Permeation

Permeation is a well-known vapor generation method usually affected by the slow penetration or permeation of a liquid sample through a polymeric membrane ⁽⁷⁾. The permeation rate of the compound is determined by:

- The physical characteristics of the membrane
- The permeability of the membrane to the compound
- The temperature of the membrane
- The partial pressure difference across the membrane
- Vapor pressure of the compound (fluid)

Under suitable conditions, permeation tubes can be used as the source of low concentrations of gases and vapors. Calibrated tubes can be purchased commercially and used to calibrate analytical instruments such as gas chromatographs. The mass flux of material is constant at a given temperature, and produces a predictable concentration as a function of the carrier flow rate. Figure 3 shows a schematic of a permeation tube generator, showing a system in which the tube temperature and flow rate are controlled in order to achieve the desired final concentration ^(8,9,10).

Controlled and predictable concentrations over a wide flow rate range are readily achievable. This requires precise and accurate amounts of analyte at usually trace levels. The generator uses small (e.g., 1/4 in. o.d.) tubes made of a suitable membrane material such as polytetrafluoroethylene (pTFE) loaded with liquid agent. The compound (permeation fluid) contacts the inside surface of the membrane and the vapor slowly permeates ⁽¹¹⁾.

When the permeation tube is held at a constant temperature a flux flow of compound vapor is emitted. This output, measured by weight loss over a suitable period of time, is the permeation or emission rate, generally expressed as nanograms per minute (ng/min). Weight loss measurements can be taken at different temperatures, producing different emission rates for the same tube. To achieve a concentration of compound lower than the emission rate, the emission flow can be diluted with a known flow of diluent gas (e.g., air or nitrogen).

The permeation method of producing vapors is not limited to instrument calibration. Higher concentrations are achievable by using larger tubes, more permeable membrane material, higher temperatures, multiple tubes, etc.

Flow Diagram Permeation Tube Apparatus (shown with disposable tube)

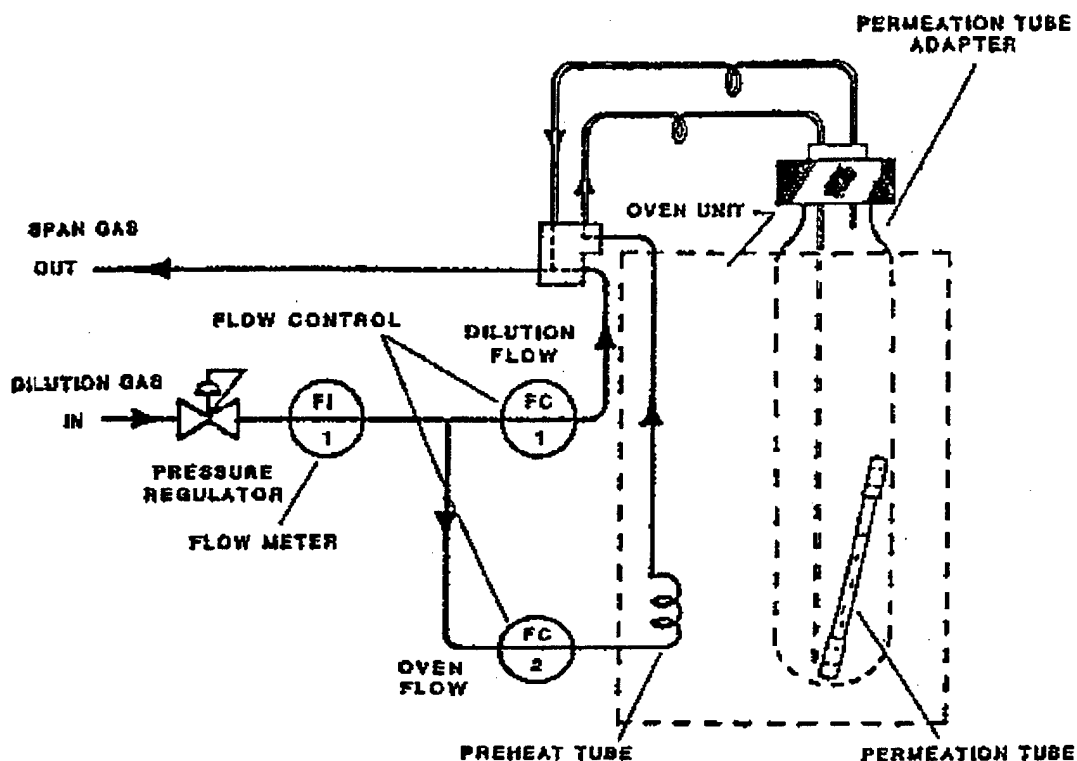


Figure 3. Schematic of Permeation Tube Vapor Generator System

2.6 Syringe Pump

The syringe pump injection method has been used for a variety of applications and is accomplished by directly injecting liquid into a carrier stream through a syringe at a fixed rate. This method has been described in detail recently by Muse and co-workers* and will not be discussed in detail in this report. Muse et al. were able to generate low-concentration streams by injecting as little as 0.1 mg/min of isopropyl methylphosphonofluoridate (GB) into an air stream at ca. 1000-1500 liter per minute flow rate for a final concentration near 0.1 mg/m³. Although lower concentrations were of interest for that work, they were more effectively generated using other methods.

*Muse, W.T., and Buettner, L.C., Generation, Sampling and Analysis of GB Vapor for Inhalation Toxicology Studies, unpublished data, March 2001.

A similar vaporization method has been effected by forcing liquid into a stream of heated air. If enough heat is applied, the liquid will be instantaneously evaporated. Ahearn and coworkers have used this method to generate high-volume streams for large item simulant testing. Using this method, concentrations of 100 mg/m^3 can readily be generated and maintained.

The vapor generator consists of a 400 cubic feet per minute (cfm) electric blower attached to the end of a length of six-inch diameter aluminum pipe. Two 208-volt heater elements are mounted inside the pipe. This length of pipe is then inserted into the side of an eight-inch diameter length of pipe roughly at a 45 degree angle. The six-inch pipe is inserted into the eight-inch pipe at least one half inch to prevent any liquid simulant from entering the pipe containing the heaters. The length of eight-inch pipe is mounted vertically in a stand. Then simulant, volume controlled by a needle valve, is pumped through an orifice mounted near the top of the eight-inch pipe to form a spray on its sides. The spray is vaporized by the hot air created by the heater elements and forced through generator by the blower motor. Temperatures of 125°F have been shown to vaporize nearly all the simulant put into the system. Since not all the simulant will vaporize, a drain must be installed in the bottom of the eight-inch pipe to recover remaining liquid for reuse. An approximate material balance can be calculated if the air flow and simulant injection and recovery rates are measured...

Simulant vapors released into the test chamber are mixed with fans to produce a uniform challenge. The feed is monitored by the system operator using miniature infrared (MIRAN) detectors and a data acquisition system. This system has been employed to generate high-flow streams for testing of the protection efficiency of unhardened collective protection shelters. These shelters typically use filtered air to generate an overpressure inside the shelter to preclude infiltration of unwanted vapors.

Another slight variation of this method is to inject low-boiling liquids directly into process streams by virtue of their own head pressure. Cyanogen chloride (CICN) is frequently used to test developmental and fielded filtration materials and systems. CICN boils at 12.8°C and therefore has an inherent vapor pressure above room temperature. Thus, it can be injected directly into process streams operating near atmospheric pressure. The flow rate of CICN is controlled using a regulator, and care must be exercised to ensure that the CICN container maintains sufficient temperature to keep its total pressure above that of the process stream. This is commonly done by equipping the CICN cylinder with a thermostated heater to offset cooling caused by the evaporation of CICN during the test.

2.7 Solid-State Vapor Generator (SSVG)

The principal method of air purification for low-volatility vapors relies on physical adsorption of vapors onto high-surface area adsorbent materials such as activated carbon. The SSVG method reverses this procedure by initially contaminating a high-surface-area material, such as activated carbon, with a small amount of the chemical of interest, i.e., chemical warfare agent or simulant. Vapor generation is effected by purging the adsorbed vapor using dry air, cylinder nitrogen, or other carrier gas through a bed packed with the adsorbent particles containing the adsorbed vapor. A schematic depiction of this generation system is shown in

Figure 4. This approach is highly effective in suppressing the equilibrium vapor pressure of the adsorbed material owing to the strong interactions between the vapors and the adsorbent. Recent studies ⁽¹²⁾ have shown that the equilibrium vapor pressure of GB is suppressed by nearly 10 orders of magnitude using a mass ratio of 1% GB to coconut-shell carbon (CSC). The degree of suppression depends strongly on the mixing (vapor loading) ratio and approaches the vapor-liquid equilibrium limit as the loading approaches the saturation limit of the adsorbent (ca. 0.4 g GB/g CSC). These observations immediately lead to the ability to precisely control the generation rate and concentration over an extremely wide range between direct generation of sub-ppT concentration levels at very low flow rates up to the VLE limit.

Solid-State Vapor Generator

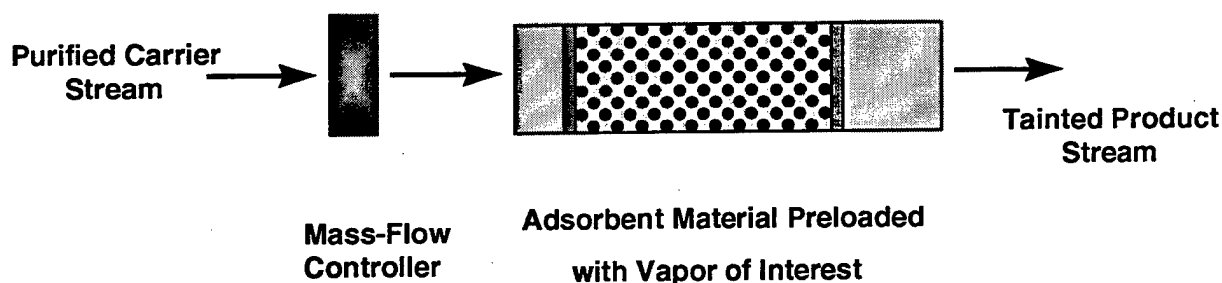


Figure 4. Schematic of Solid-State Vapor Generator

In the previous work, a generation rate of 100 femtograms per minute for GB (b.p, 158°C) was observed, and the generation rate measurements were only limited on the low end by the detection technology used, not by the generator conditions (loading ratio and temperature, primarily) which could have been reduced further.

It should also be noted that SSVG vapor phase concentrations can be accurately predicted based on well-known adsorption equilibrium correlations using this generation method. One of the most widely used is the well-known DR (Dubinin-Radushkevich) correlation. While it is well known that the DR correlation does not capture the low concentration (Henry's Law limit) range accurately, the low-concentration point at which the correlation loses fidelity for medium-volatility vapors is unknown. A number of studies had established a low-concentration limit for this type of investigation in the 10^{-6} relative pressure range. Recent work from ECBC has demonstrated that the DR correlation accurately describes GB adsorption equilibrium on CSC down to relative pressures in the 10^{-10} range.

2.8 Humidification

It is frequently desirable or necessary to generate vapor streams using air as the carrier to simulate an operational environment. In this case an added complication arises due to the interaction between water vapor and the vapor of principal interest. Ideally, Raoult's Law limits the sum of the relative pressures (ratio of partial pressure to single-component vapor pressure at the measurement temperature) of all vapors in a mixture to 1.0. For example, an air stream at 50% RH can only hold up to 0.5 relative pressure of the vapor of interest. Deviations from Raoult's Law can be significant, especially for mixtures involving non-miscible liquids.

The conditioning side of the saturator described in section 2.2.1 and Figure 1 above will be described as an example of a humidification method. The humidification stream uses the flow from flow meter (19) that is set equal to the combined flows through flow meters (8) and (11). This dry air stream is combined with the flow from flow meter (20) that is set equal to the flow from flow meter (12), through the humidifier (21), to form the conditioning air stream. This stream is also split into two streams similar to that described in the chemical vapor generation section. One stream passes through the regulating valve (22) and is released. The other stream is directed to solenoid (B), through solenoid (C) into the sampling cup (17) while the solenoids are not energized. Challenge with the chemical vapor is effected when the three solenoids (14) are energized. The conditioning air stream exhausts through solenoid (C); through a regulation valve (23); to the RH and temperature indicator (24) for an indication of the RH and temperature conditions. This arrangement permits a wider range or regulation of flows to meet the test demand. Because flows for controlling humidity of the two sections are matched with identical flow rates, readings obtained from the humidity indicator can be considered as equal to the RH condition of the chemical vapor generating section.

To assure that the air is saturated when it passes through the water reservoir kept at the same temperature as the environment, the flow is kept at minimum permissible to provide adequate volume for the demand (e.g., 3 liters per minute is adequate for most detectors). The saturation efficiency needs to be considered when higher flows are used, however. By keeping the humidifier water at the same temperature with the environment, the relationship will hold. The air passing through the humidifier can only become saturated at the same temperature and thus, when it is mixed with the dry air, the percentage of RH is directly proportional to the dilution. This technique minimizes the need to manipulate flow adjustments to control the RH when a heated water source is employed. It also eliminates the condensation problems associated with heated water or steam injection techniques.

Similar methods have been used by other workers. Often the test dew point is not controlled, but simply monitored along with testing temperature in order to assess RH. Interestingly, several applications are more sensitive to dew point, i.e., water mole fraction, than RH. An exception to this is filter testing, where RH more often correlates to performance than dew point.

3. Discussion

The advantages of each method for generating vapors will be discussed in turn.

Spargers have been widely used for generation of high-flow stream. This method has general utility, but is subject to unintended release of liquid in the event of pressure transients downstream of the generator. This possibility presents a serious problem for generation of high-toxicity vapors, and extraordinary safety measures (e.g., pressure relief valve and liquid trap) must be used to preclude liquid release when used for CW agent vapor generation.

Another difficulty experienced when using the sparger method is the possibility of unintended aerosol production and transport with the vapor. Expedient measures can be implemented to remove aerosols from the product stream, including aerosol filtration and maintaining the sparger at sub-ambient temperature; however, this phenomenon reduces the operator's ability to establish predictable correlations between concentration and generator operating conditions.

The use of delta tube saturator and the two-stage dilution system described above has the capability to generate highly purified agent vapor in a small controlled volume of conditioned air within the limits imposed by their physical properties. The small quantity of agent permits it to rapidly purge the higher-volatility impurity materials that may interfere with the generation of the vapor of interest.

The delta tube behaves similarly to a diffusion-controlled generator except with additional control related to operation at saturation, i.e., does not depend on flow dynamics, which can occasionally be unpredictable. The flow rate of the carrier gas can be precisely controlled using a needle valve. More importantly, the use of the delta tube prevents the dangerous back-splashing of agent that can occur when an impinger is used improperly.

The use of two-stage dilution system expands the range of achievable concentrations while keeping the final dilution flow rate to a minimum as required by the experiment and safety considerations without having to resort to high volume dilution to reach low concentration generation. The two-stage system also facilitates generation and control of relative humidity and vapor concentrations.

The saturator systems can produce the desired concentration very rapidly. In cases where higher generation rates are needed, a higher capacity multiple-pass saturator as shown in figure 2 or parallel addition of delta tube(s) together with higher bath temperature can be implemented. This approach has been used recently to measure the vapor pressure of CW agents⁽⁵⁾ as well as to generate vapors for filter testing and other analytical purposes, e.g., detector calibration. The delta tube system has been used to generate total flow rates as high as 2 liter/minute.

The advantages of the permeation tube methods include:

- Dynamic blending of components and using while fresh

- Measurements (temperature and weight) are traceable to NIST primary standards and not dependent on analysis by instruments which are subject to calibration accuracy
- Concentration can be accurately and predictably varied by changing dilution flow rate or operating temperature
- Carrier gas and humidity can be varied according to requirements of the intended application
- Permeation tubes are safer to handle than neat liquid
- Low flux rates are suitable for calibrating high-sensitivity detection systems

Syringe Pump methods work well and are generally applicable for a wide variety of materials, however this method has advantages and limitations, which should be recognized by the potential user. Containment difficulties arise for low-boiling liquids. Also, the ability to generate vapors at very low rates is limited currently to greater than 0.1 milligram/minute (0.1 microliter/minute) by available equipment. Additionally, since this method involves liquid injection, care must be taken to ensure that complete evaporation and mixing are achieved prior to sampling the product stream. Cooling due to liquid evaporation can be an exacerbating factor for the latter, particularly at high injection rates owing to the low heat capacity of air. For example, injection of liquid water into a dry air stream at 25°C to achieve 10% RH product will result in a stream at ca. 19°C and 15% RH unless the stream is reheated to restore the original temperature. This effect will be less significant for low-humidity, low-flow conditions since the heat of evaporation will be low, but will become more pronounced at high-flow, high-humidity conditions, which involve more heat of evaporation and tend to be more adiabatic.

Permeation tube generators are predictable, safe, and convenient to operate. The two principal disadvantages are the low generation rates as compared to saturator methods and the limited range of compounds, which can be used. VX, for example, has not been generated using a permeation tube owing to the failure, so far, to identify a containment material with appropriate physical and chemical properties to effect the desired permeation rate and system stability.

The SSVG method is ideally suited for direct generation of low flux, i.e., low concentration and low flow rate, streams without the need for further dilution. Another potential advantage of this method, which has not been explored yet, is the ability to reduce the head pressure over a high-volatility vapor or gas that might normally be dispensed from a high-pressure container. This safety feature might be particularly useful for field dissemination of CW agents such as cyanogen chloride and arsine for detector calibration, but should realize its greatest utility in industrial applications such as gas (hydrogen) storage. The wide range of generation rates and control parameters available using this method make it ideal for a wide range of applications. In addition, storage of highly toxic vapors on a solid adsorbent can significantly reduce the safety risks associated with handling these materials.

Potential problems associated with the SSVG method include decomposition of the adsorbate as a result of intimate contact with adsorbent reactive sites. This effect has been observed for adsorbed HD and VX, recently and seems to be exacerbated by the presence of water vapor. Efforts to minimize this effect include use of low-ash adsorbents, operating at as low a temperature as possible, and avoiding the presence of water. The latter includes sample preparation methods to reduce water contamination and use of ultra-dry carrier streams since even part-per-million range water vapor in the carrier will eventually be concentrated on the surface of the adsorbent and potentially lead to hydrolysis.

The high-pressure vapor injection method has the distinct advantage that a known dose of chemical is delivered to the test rig. Also, the integrated concentration-time (Ct) challenge can be determined if the flow rate is known. Often, however, test planners desire step function challenges, i.e., rapid establishment and removal of the feed concentration over the test duration. In the present case, the feed concentration rises rapidly but tails off slowly due to mixing effects inside the mixing chamber. On the other hand, this injection method more closely approximates what might be expected under field dissemination. In fact, mixing effects in the field will most likely be more pronounced than observed in this test configuration.

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